

Integration of a calcium looping system for CO₂ capture in an existing power plant

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ABSTRACT

This work analyses a Ca-looping system that uses CaO as regenerable sorbent to capture CO₂ from the flue gases generated in an existing supercritical power plant. The CO₂ is captured by CaO in a CFB carbonator while coal oxycombustion provides the energy required to regenerate the sorbent. Part of the energy introduced into the calciner can be transferred to a new supercritical steam cycle to generate additional power. Two case studies based on a scenario of low solid circulation rate between reactors have been integrated with the new supercritical steam cycle. Efficiency penalties, mainly associated with the energy consumption of the ASU, CO₂ compressor and auxiliaries, can be as low as 7.5 percentage points of net efficiency when working with low CaCO₃ make-up flows and integrating the Ca-looping with a cement plant that makes use of the solid purge. 70 % of the CO₂ generated in the existing plant is captured under these conditions; with an overall CO₂ capture over 86 %.

INTRODUCTION

CO₂ capture and storage (CCS) has been identified as a potential technology to continue using fossil fuels in a CO₂ emission constrained world. Among the different CCS technologies, post-combustion ones are the only options for the retrofitting of existing power plants. We refer here to those recently built or under construction, as those that are too old and with low efficiency are not suitable for CCS [1]. Amine-based processes have been proved commercially for post-combustion CO₂ capture systems [1, 2], but the need of optimization and scale up that still require encourages the development of emerging post-combustion technologies using alternative solvents or solid sorbents [1].

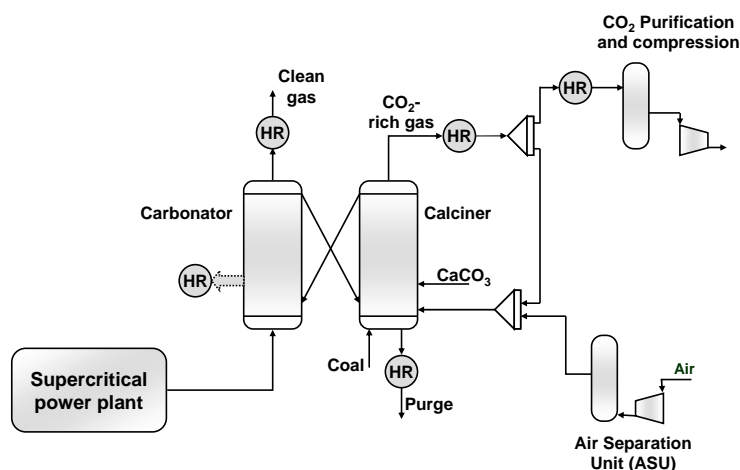


Figure 1. Scheme of the Ca looping system integrated with the supercritical power plant. (HR: Heat Recovery)

Some papers in the literature describe highly integrated systems to minimize the energy penalty that include the modification of the operation conditions in the turbines and water heaters of the original plant [10]. Few papers deal with the integration of a Ca looping system into an existing power plant not involving operational modifications that affect its functioning. Romeo et al 2008 [11] proposed the integration of this capture system, operating at a fixed conditions to achieve 85 % CO₂ capture, with a supercritical coal-fired power plant including a new supercritical steam cycle. Recently mass and energy balances of a Ca looping system integrated with a supercritical steam cycle have been solved studying the

economical impact of solids purging on the tonne CO₂ avoided cost [12]. It was concluded that the amount of purged material had great effect on the cost of CO₂ avoided, and, although it was always competitive with respect to other technologies, it was minimized by working with low purge streams. Ca-looping operation conditions have proven critical for defining the heat requirements in the calciner and the overall performance of the system [6] and they are heavily interlinked with external variables such as the make-up flow and the solid circulation rate between reactors. The purpose of the present work is to design suitable configurations to carry out the energy integration of a Ca looping cycle implemented in an existing supercritical coal-fired power plant. Mass and energy balances of the Ca looping system are solved, including realistic models for the carbonator reactor in order to select the conditions for thermal integration with a new supercritical steam cycle. An Aspen Hysys® model of the coal-fired supercritical power plant plus the capture system has been developed and the efficiency penalty owing to the capture and CO₂ compression system has been estimated as a function of operating conditions.

PROCESS SIMULATION MODEL

The Aspen Hysys® simulation model includes a Ca looping system integrated with an existing supercritical power plant with 45 % net efficiency producing an output of 438 MW. This power plant burns 200 tonnes per hour of coal with a 15 % of air excess. The flue gas is heat exchanged with the coal and air streams entering the boiler and then is sent to a desulphurization unit that removes the 90 % of the SO₂ in the flue gas. Once the flue gas has been cooled and SO₂ removed, it is recompressed and fed to the carbonator in the Ca looping system. The flue gas enters the carbonation unit with a mass flow of 446 kg/s, at 180 °C a CO₂ content of 14.5 %v and 0.04 %v of SO₂. The carbonator and the calciner have been implemented in the simulation model as circulating fluidized bed reactors operating at steady state and at atmospheric pressure.

The carbonator has been designed to operate at 650 °C. To refine the mass balances of the system from Fig. 1, a reactor model for the carbonation unit based on simple assumptions about the fluid-dynamics has been included. It integrates the existing knowledge on sorbent capture capacity and reactivity. The main purpose of the model is to calculate CO₂ capture efficiencies in the carbonator unit, E_c , as a function of operational and design conditions:

$$E_c = \frac{\text{CO}_2 \text{ reacting in the carbonator}}{\text{CO}_2 \text{ in the flue gas entering the carbonator}} = \frac{F_{CaO}}{F_{CO_2}} X_{carb} \quad (1)$$

where F_{CO_2} is the molar flow rate of CO₂ entering the carbonator, F_{CaO} the molar flow rate of CaO circulating between calciner and carbonator, and X_{carb} the conversion reached by the sorbent in the carbonator.

The structure of the model and resolution method is similar to the model proposed by Alonso et al. [13] but it incorporates new features regarding the carbonation reaction model and the CO₂ carrying capacity of CaO particles partially converted through the cycles. The overall mass balances in the system can be written as:

$$\text{CO}_2 \text{ reacting with CaO in the bed} = \text{CO}_2 \text{ removed from the gas phase} = \text{CaCO}_3 \text{ formed in the circulating stream of CaO} \quad (2)$$

The model is solved when the terms from the equation above are calculated for a determined set of operation and design conditions. It is considered the instantaneous and perfect mixing of the solids, in both carbonator and calciner, and the plug flow for the gas phase in the carbonator. The reactor model includes a recently developed carbonation model based on Bathia and Perlmutter's kinetic model [14] which assumes that carbonation reaction takes place in two stages and adapted to multiple reaction cycles [15]. The first stage is controlled by chemical reaction and the second stage is controlled by both chemical reaction and product diffusion through the product layer of the CaCO₃ formed. The general reaction rate expression is:

$$r = \frac{k_s S(1-X) \sqrt{1-\Psi \ln(1-X)}}{(1-\varepsilon) \left[1 + \frac{\beta Z}{\Psi} (\sqrt{1-\Psi \ln(1-X)} - 1) \right]} C \quad \text{with} \quad \beta = 2k_s a \rho_{CaO} (1-\varepsilon) / M_{CaO} b D_p S$$

(3)

$X=X_{kd}$ and $\beta=0$ for $t < t_{kd}$; $X=X_N$ for $t > t_{kd}$. t_{kd} is the residence time that marks the change in reaction regime from kinetic control to kinetic plus diffusional control. This change in reaction regime takes place when the product layer reaches a characteristic thickness of 38 nm and the sorbent presents a conversion X_{kd} [15]. X_N is the maximum carbonation conversion of a CaO particle as function of the number of carbonation calcination cycles. To solve the reaction model it is necessary to include information on sorbent structural parameters (S , $\Psi=4\pi L(1-\varepsilon)/S^2$), and reaction kinetics (k_s , D_p) [15]. In the system of Fig. 1 with an interconnected perfect mixed reactors with a flow of solids circulating between them, and a continuous fed and purge, there will be a large population of particles that have been cycling between reactors a different number of times and therefore present a different CO₂ capture capacity (X_N) and reactivity. Therefore, the sorbent entering the carbonator unit should be better described as an average sorbent able to convert up to X_{ave} on each cycle following r_{ave} reaction rate. X_{ave} will take into account the distribution of number of cycles that experiences the sorbent as a function of sorbent molar make-up flow (F_0), F_{CaO} and the fact that the particles may not achieve its maximum conversion on every cycle [16]:

$$X_{ave} = \frac{a_1 f_1^2 F_0}{F_0 + F_{CaO} f_{carb} (1 - f_1)} + \frac{a_2 f_2^2 F_0}{F_0 + F_{CaO} f_{carb} (1 - f_2)} + b \quad (4)$$

Where a_1 , a_2 , f_1 , f_2 and b are fitting constants extracted from Li [17]. Eq (4) allows estimating, through an iterative process, the average maximum conversion that is able to achieve a particle of CaO in the carbonation reactor when the mean carbonation extent of the particles is f_{carb} .

The average sorbent carbonation capacity X_{ave} , can be directly linked with the specific reaction surface of the sorbent through the carbonate layer that is formed on the available pore surface. It is therefore possible to estimate the average specific reaction surface S_{ave} that presents the sorbent entering the reactor. The rest of the sorbent structural parameters required to incorporate in the reaction model can be also extrapolated from X_{ave} [15].

The model needs a set of input conditions as the solids inventory in the carbonator, F_0 and F_{CaO} that allow to calculate the average activity of the sorbent entering in the reactor (X_{ave}) and the average particle residence time in the carbonator. To solve the model it is supposed a fraction of solids in the reactor, f_a , with a residence time below t_{kd} , that it is reacting under kinetic control. For a perfect mixed reactor f_a can be represented as:

$$f_a = (1 - e^{-t_{kd}/\tau}) \quad (5)$$

where τ is the average CaO particle residence time in the carbonator calculated as the molar inventory of CaO in the carbonator divided by the molar flow of CaO entering the reactor. The rest of the CaO particles will react under combined kinetic and diffusion regime. The model is solved through an iterative process on f_a that allows calculating E_c by two parallel routes and ends when both routes yield the same E_c . The first route to calculate E_c is obtaining the conversion of the solids X_{carb} to introduce it in Eq. (1):

$$X_{carb} = f_a X_{t < t_{kd}} + (1 - f_a) X_{t > t_{kd}} \quad (6)$$

where

$$X_{t < t_{kd}} = \frac{\int_0^{t_{kd}} r_{ave,t < t_{kd}} t \frac{1}{\tau} e^{-\frac{t}{\tau}} dt}{f_a} \quad \text{and} \quad X_{t > t_{kd}} = X_{kd-ave} + \frac{\int_{t_{kd}}^{\infty} r_{ave,t > t_{kd}} t \frac{1}{\tau} e^{-\frac{t}{\tau}} dt}{(1 - f_a)} \quad (7)$$

The second route to calculate E_c is through the carbon mass balance in the gas phase. In this case the carbonation efficiency, E_c , is calculated at the exit of the reactor. To do so the integrated form of Eq. (8) is applied:

$$F_{CO_2} \frac{dE_c}{dz} = A \frac{\rho_{CaO}}{PM_{CaO}} \left[f_a r_{ave_{t < t_{kd}}} + (1 - f_a) r_{ave_{t > t_{kd}}} \right] \quad (8)$$

The calciner has been designed as an adiabatic oxy-coal combustor reactor operating at 950 °C. This temperature allows considering complete calcination of the $CaCO_3$ even under rich CO_2 atmosphere. The combustion of coal in this reactor supplies the energy required to calcine the $CaCO_3$ and to heat up the stream of solids entering the reactor. The O_2 to burn the fuel is supplied by an air separation unit (ASU). Part of the CO_2 -rich stream is recirculated to the reactor, to maintain an inlet concentration of 25%(v) O_2 . It has been considered that 40 % of the ashes of the coal burnt in the calciner are separated as fly ashes in the secondary cyclones in the calciner together with a 5 % of unburned material.

SIMULATION RESULTS

A simulation exercise has been carried out covering a range of CO_2 capture efficiencies in the carbonation unit from 70 to 90% of the CO_2 generated in the existing power plant. To solve these balances the CaO inventory in the carbonator has been fixed between 1500-2000 kg/m^2 , with a flue gas flow rate of 6 m/s through this reactor. For each case study, the ratio F_0/F_{CO_2} has been varied from 0.1 to 0.35 and the ratio F_{CaO}/F_{CO_2} has been adjusted to reach the E_c considered. Fig. 2 shows the results from the reactor model implemented in the carbonator. It represents the conversion of CaO particles, X_{carb} , as function of fresh sorbent make-up flow and solids recirculation between reactors for different E_c . Left hand side axis represents the conversion of CaO particles in the reactor that is always lower than their maximum carbonation conversion calculated through Eq. (4) and is represented in the right hand side axis. The difference $(X_{ave} - X_{carb})$ represents the fraction of CaO that was originally active in the calcined stream of solids entering the carbonator and that has not been yet converted to $CaCO_3$. As it can be seen from Fig. 2 (left) once a fresh sorbent make-up flow is fixed, higher circulation rate of solids is required to increase carbonation efficiency E_c in the reactor. It can be also seen that increasing the fresh sorbent addition results in a more active sorbent able to reach higher carbonation conversions.

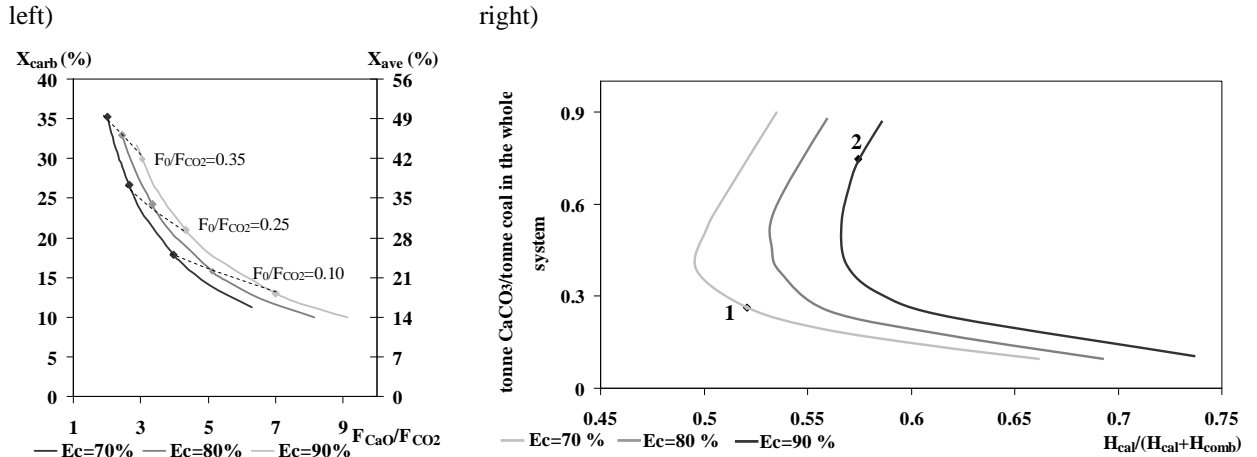


Figure 2. left) Carbonation conversion of CaO particles in the carbonator as a function of F_{CaO}/F_{CO_2} and F_0/F_{CO_2} , for different E_c . right) Energy fraction consumption in the calciner ($H_{cal}/(H_{cal}+H_{comb})$) as a function of fresh $CaCO_3$ make-up flow and E_c in the Ca looping system.

Incorporating the results from the carbonator model, the simulation model in Aspen Hysys calculates the fuel requirements in the calciner unit as well as O_2 consumption, the compression work required, and the composition of every stream in the process as well as the energy available. Figure 2 right) shows the fuel requirements of the calciner unit (H_{cal}) with respect to the power plant (H_{comb}) as function of sorbent consumption for the range of carbonation efficiencies analysed. The ratio $H_{cal}/(H_{cal}+H_{comb})$ has been calculated considering the chemical energy based on the lower heating value of the coal. It can be observed that there is a minimum consumption of coal in the calciner corresponding to a minimum calciner size that sets the limit between sorbent activity maintained with high $CaCO_3$ make-up flow or with high solid circulation rates between reactors. These coal and $CaCO_3$ consumptions allow different strategies of design and operation. The scenario proposed in this work is a Ca-looping system working with low solid circulation rates between carbonator and calciner ($F_{CaO}/F_{CO_2} < 4$). In this scenario, two different case studies have been selected to implement the energy integration with a new steam cycle varying the fresh sorbent consumption. A first case with a low $CaCO_3$ consumption of $F_0/F_{CO_2} = 0.1$ (point

1 in Fig. 2 right) yields a carbonation efficiency, E_c , of 70 %. The second case with a CaCO_3 consumption of $F_0/F_{\text{CO}_2}=0.35$ (point 2 in Fig. 2 right) yields a 90 % of carbonation efficiency. The global CO_2 captured in both cases, taking into account the CO_2 captured from the original power plant plus the CO_2 generated in the calciner, is over 85 %. The energy availability in these two simulation cases of the Ca looping system will determine the integration with the new steam cycle that optimizes the thermal efficiency of the system.

The energy in the gas and solid streams at high temperature can be used to produce supercritical steam at 600°C and 280 bar that generates additional power in a steam cycle. The energy sources in the Ca looping system according to the scheme in Fig. 1 (pointed as *HR* in Fig. 1) are:

1. The rich CO_2 gas stream that leaves the calciner at 950°C and is cooled down to 80 °C in different stages before being purified and compressed
2. The energy released in the carbonator due to the carbonation reaction and the cooling of the solids from the calciner at 950°C
3. The energy in the gas leaving the carbonator at 650°C that could be cooled down to 100-120°C before being sent to stack
4. The solid purge in the calciner that could be cooled down before being used in the cement industry or being disposed

The heat requirements in the new supercritical steam cycle are located in six zones at different temperature range: economizer, steam generator, superheater, reheater, high pressure and low pressure water heaters. 600°C is the highest temperature in the steam cycle and is located in the superheater and in the reheater where steam is heated from 415°C and 325°C respectively. The economizer heats the water coming from the high pressure water heaters at 280°C to 400°C before entering the steam generator. In order to maximize the steam generation the economizer has been divided into two stages working at different temperatures. The steam turbine of the supercritical steam cycle has two high pressure bodies, two medium pressure bodies and a low pressure body with five stages. Detailed operating conditions of the supercritical steam cycle considered could be found in literature [18].

The energy availability in the Ca looping system varies with the operating conditions, the aim of the case studies has been to maximize the steam generation at the same time that 600°C is maintained in the superheater and in the reheater. Heats recovered from the CO_2 -rich stream in the calciner and from the carbonator represent the main energy inputs for the steam cycle. Both energy streams are suitable to be integrated into the superheater and reheater owing to their high temperature energy availability. The energy requirements in the superheater exceeded, in the simulated cases, the energy available in the carbonator. Therefore, the configuration that this work proposes consists of introducing in the superheater the energy available in the CO_2 -rich stream ($Q_{\text{rich CO}_2}$), according to heat exchanger temperature levels. Then the energy from the carbonator ($Q_{\text{carbonator}}$) will be split for introduction into the one-through steam generator (boiler) and into the reheater. The energy share-out between these two pieces of equipment will lead to a certain amount of steam in the cycle. So, if 600°C is maintained in the reheater, the steam in the cycle will be maximized in order to gain as much efficiency as possible. The remaining energy still available in the CO_2 -rich stream (after its integration with the superheater) will be used in the high temperature stage in the economizer. Energy in the gas leaving the carbonator at 650°C ($Q_{\text{clean gas}}$) is integrated in the low temperature stage into the economizer, where it is cooled down to 300°C. The outlet temperature of the clean gas in the first economizer will be always the same in order to maintain 20°C difference between the temperature of this stream and the temperature of the water incoming the economizer. Therefore, the steam generated in the boiler will determine the energy needed in the second stage in the economizer and the temperature level for the remaining energy streams. Once the main energy fluxes are integrated following the layout represented in Fig. 3 left, there will be low temperature energy available in the CO_2 -rich stream, the CO_2 -rich stream to purification, in the clean gas stream and in the solids purge. Depending on this energy availability, the number of steam bleeds in the steam turbine can be reduced.

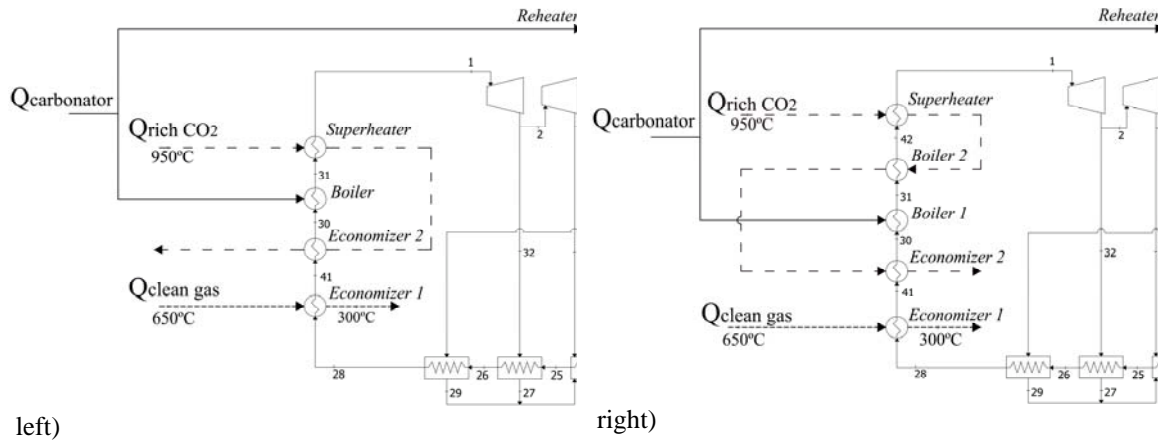


Figure 3. Thermal integration between the Ca looping system and the supercritical steam cycle. Left) simulation case 1; right) simulation case 2.

The thermal integration explained applies to the case study represented as point 1 in Fig. 2 right. When fresh sorbent addition is high ($F_0/F_{CO_2}=0.35$, point 2 in Fig. 2 right) the energy requirements in the calciner increase the ratio $H_{cal}/(H_{cal}+H_{comb})$ up to 0.57. In this case the energy in the CO_2 stream exceeds the energy recovered from the carbonator. The thermal integration depicted in Figure 3 left needs to be modified and part of the energy in the CO_2 -rich stream is used to generate additional steam in a second steam generator as in Figure 3 right.

As a result of the thermal integration between the CO_2 capture plant and the new supercritical steam cycle additional power is generated, $W_{supercritical_cycle}$. The net power output of the system comprising the existing power plant and the Ca looping system was calculated according to Eq. (9).

$$\eta_{net} = \frac{W_{existing_plant} + W_{supercritical_cycle} - W_{ASU} - W_{CO2compressor} - W_{auxiliaries}}{H_{cal} + H_{comb} - H_{calF0}} \quad (9)$$

$W_{existing_plant}$ and $W_{supercritical_cycle}$ are the net power output of the existing power plant and the new supercritical steam cycle respectively. H_{cal} and H_{comb} represent the chemical energy introduced by coal in the system. Eq. (9) considers the integration of the purged material within a cement manufacture process. In this case, H_{calF0} , the energy associated with the calcination of the $CaCO_3$ make-up flow, should be discounted from the chemical energy introduced in the system. The energy consumed by the ASU, the CO_2 compressor (200 kWh/tonne O_2 , and 100 kW/tonne CO_2 respectively [1]) and the usual power plant auxiliaries (2% of the gross power output of the new steam cycle) and fans needed for solids circulation has been considered to calculate the net efficiency of the system. The net thermal efficiencies, included in Table 1, are 37.5 % for the 70% E_c case and 34.8% for the 90% E_c case. This last case presents the highest ASU consumption, as it requires a higher amount of coal in the calciner (see Fig. 2 right), and also the highest CO_2 compression work. The consumption of a higher amount of fresh $CaCO_3$ in the Ca-looping cycle, together with higher carbonation efficiency in the carbonator contribute to increase the CO_2 molar flow to be compressed. These two factors increase the CO_2 compression work with respect to the case presenting lower E_c .

Table 1. Thermal efficiencies and main consumptions in the simulation cases from Figure 2 right.

	η_{net} (%)	W_{ASU} (MW_e)	$W_{CO2compressor}$ (MW_e)	Penalties (%)
E_c 70 %	37.5	63	66	7.5
E_c 90 %	34.8	78	90	10.1

To evaluate energy penalties associated with the capture system, a reference plant consisting of a supercritical power station with an energy input ($H_{comb}+H_{cal}$) and 45 % net efficiency is considered. The energy penalties with respect the reference plant, included in Table 2, could be as low as 7.5 percentage points for the case capturing 70% of the CO_2 generated in the existing power plant. It is important to highlight that although this capture efficiency in the carbonator may seem conservative, the global CO_2 captured in the process: existing power plant plus Ca-looping cycle is 86%. Global CO_2 capture efficiencies over 96% can be achieved when 90% of the CO_2 generated in the existing power plant is

captured with an energy penalty of 10.1 percentage points. The thermal integration proposed in this work applies to a scenario of a Ca-looping cycle with low solid circulation rate between reactors. It is important to highlight that, according to Fig 2 right, scenarios with high circulation rates between reactors could be also proposed to achieve a determined E_c . In this case the optimal thermal integration, and thermal efficiencies for the new scenarios should be evaluated as the energy availability in the process streams and the consumptions of the main equipments in the process would be different.

CONCLUSIONS

The energy sources from a Calcium looping system can be integrated into a supercritical steam cycle to produce additional power output. The thermal integration of these energy sources with the equipments in the steam cycle is strongly linked with the operating conditions of the capture system. The scenario proposed in this work is a Ca-looping cycle working with low solid circulation rates between reactors. Two simulation cases varying fresh sorbent addition, and therefore the capture efficiency achieved in carbonator, have been selected to carry out the thermal integration. The net thermal efficiencies of the simulated cases were 37.5 % for a system capturing 70 % of the CO_2 from the existing power plant and 34.8% efficiency for a system capturing 90% of the CO_2 generated in the existing power plant. In both cases the overall CO_2 capture of the process is over 86 %.

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NOMENCLATURE

a, b = stoichiometric coefficients for carbonation reaction
 C = bulk concentration of CO_2 kmol/ m^3
 dz = differential bed height (m)
 D_p = apparent product layer diffusion coefficient, m^2/s (see Ref. 15)
 H = chemical energy introduced in the system (MW), comb relative to existing power plant; cal relative to calciner, calF0 associated to calcination of fresh sorbent make-up flow
 k_s = rate constant for surface reaction, m^4/kmols (see Ref. 15)
 L = total length of the pore system, m/m^3 (see Ref. 15)
 M_{CaO} molecular weight of CaO kg/kmol
 Q = energy available (MW): carbonator in the carbonator unit; clean gas in the clean gas stream; rich CO_2 in the gas stream exiting the calciner
 r = general carbonation reaction rate expression, ave relative to average particle (see Ref. 15)
 S = reaction surface, ave relative to average particle, m^2/m^3 (see Ref. 15)
 X = CaO molar conversion; N relative to cycle N; ave relative to average particle; kd transition between reaction regimes (see Ref. 15)
 Z = ratio volume fraction after and before reaction (see Ref. 15)

Greek letters

ε = porosity
 ρ_{CaO} = CaO density, kg/m^3

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